Chapter 3.5: Classical degrees of freedom

6N continous variables

classical microstate $\{\vec{r}_1, \vec{p}_1, \vec{r}_2, \vec{p}_2, \vec{r}_3, \vec{p}_3, ..., \vec{r}_N, \vec{p}_N\}$, phase space integration: $\prod_j d^3\vec{r}_j d^3\vec{p}_j = d\Gamma^{6N}$ $\left(\times \frac{1}{N!}\right)$

More general: $\{q_1, q_2, q_3, q_4, ...\}$ with energy $\varepsilon(q_1, q_2, q_3, q_4, ...)$ (not necessarily independent)

general canonical degrees of freedom which are continuous

Integration: $d\Gamma = \prod_j dq_j$ $\left(\times \frac{1}{N!}\right)$

Consider : $\left\langle q_j \frac{\partial \varepsilon}{\partial q_k} \right\rangle = \frac{1}{Z} \int d\Gamma \, q_j \frac{\partial \varepsilon}{\partial q_k} e^{-\beta\varepsilon}$ $= -\frac{1}{\beta Z} \int d\Gamma \, q_j \frac{\partial e^{-\beta\varepsilon}}{\partial q_k}$

$u \qquad v'$

$$= +\frac{1}{\beta Z} \int d\Gamma \frac{\partial q_j}{\partial q_k} e^{-\beta\varepsilon} \cancel{- \frac{1}{\beta Z} q_j e^{-\beta\varepsilon} \Big|}$$

$\varepsilon \to \infty$ as $p \to \infty$ or $r \to \infty$ or periodic boundaries

$-u' \quad v \qquad - uv\Big|_{\text{boundaries}}$

$$= \frac{1}{\beta} \left\langle \frac{\partial q_j}{\partial q_k} \right\rangle = \underline{\underline{k_B T}}$$

Def. 3.4: The virial theorem for statistical mechanics states, that for continuous classical variables

$$\left\langle q_j \frac{\partial \varepsilon}{\partial q_k} \right\rangle = \delta_{jk} k_B T$$

prerequisite: $\varepsilon \to \infty$ at "boundaries"

or q_j periodic

Special case: Bilinear energy $\varepsilon = \sum_{jk} A_{jk} q_j q_k = \sum_j \varepsilon_j$ where $\varepsilon_j = q_j \sum_k A_{jk} q_k$

$A_{jk} = A_{kj}$ (double counting)

$$\frac{\partial \varepsilon}{\partial q_l} = \sum_{j \neq k} \left(A_{jk} \frac{\partial q_j}{\partial q_l} q_k + A_{jk} q_j \frac{\partial q_k}{\partial q_l} \right) + \sum_j A_{jj} \frac{\partial q_j^2}{\partial q_l}$$

$\frac{\partial q_j}{\partial q_l} = \delta_{jl}$

$$= 2 \sum_k A_{lk} q_k$$

$$\varepsilon_j = q_j \sum_k A_{jk} q_k = \frac{1}{2} q_j \frac{\partial \varepsilon}{\partial q_j}$$

Def. 3.5: The equipartition theorem for statistical mechanics states, that for an classical energy $\varepsilon_j = \sum_j \varepsilon_j$ with $\varepsilon_j = \sum_k A_{jk} q_j q_k$

also possible by using change of variables

or by solving for eigenmodes (diagonal form of A_{jk})

$$\langle \varepsilon_j \rangle = \frac{1}{2} k_B T = \frac{1}{2} \left\langle q_j \frac{\partial \varepsilon}{\partial q_j} \right\rangle = \frac{1}{2} k_B T$$

Virial

specific heat $C = \frac{\partial \langle \varepsilon_j \rangle}{\partial T} = \frac{1}{2} k_B$

ideal gas $\varepsilon = \sum_j \frac{p_j^2}{2m}$ 3N momenta

$$E = \langle \varepsilon \rangle = \frac{3}{2} N \cdot k_B T$$